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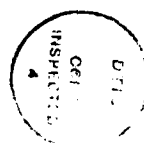
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**Depolarized Light Scattering and
Dynamic Shear Compliance of
Viscoelastic Liquids**

C. H. Wang
Department of Chemistry
University of Nebraska
Lincoln, NE U.S.A. 68588-0304



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Abstract

Efforts are made to relate the depolarized light scattering spectral power density to the dynamic shear compliance spectrum of a viscoelastic liquid. Generalized Langevin equations are used to describe the dynamics and coupling of reorientation and translational motions. It is shown that in the presence of the coupling, the depolarized scattering spectrum consists of two components, one is associated with the reorientational motion, and the other with the viscoelastic relaxation of the solution. Methods to obtain the dynamic shear compliance from the depolarized light scattering spectrum are described. It is also shown that in the limit of very slow reorientational motion, the depolarized light scattering spectrum is proportional to the imaginary part of the dynamic compliance spectrum, a result predicted by the Pockels photoelastic law.

I. Introduction

Relating the dynamic light scattering spectral density to the mechanical relaxation spectrum is an important area of research. Making the correlation brings about the unification of information that is currently obtained separately by the two techniques, hence enabling one to seek the desired physical data with one technique when the other becomes inconvenient or failed. The dynamic light scattering spectral density in a bulk liquid occurs as a result of the thermally induced modulation of the dielectric constant tensor due to local density and orientational fluctuations of molecules inside the scattering volume. If the bulk liquid is a polymer, the local density and orientational fluctuations are associated mainly with the motion of chain segments. On the other hand, mechanical relaxation occurs as a result of segmental motion and as such it is expected to be related to dynamic light scattering. Both the local density fluctuations and the orientational fluctuation contribute to the polarized (VV) component of the scattered light, whereas the depolarized (VH) light scattering intensity is associated with the orientational fluctuation.

In an one component system, it has been shown that the dynamics of density fluctuation is equivalent to the relaxation of longitudinal compliance.¹ Consequently, dynamic light scattering serves as an alternative technique to measure the longitudinal compliance spectrum, which has generally been obtained by a mechanical relaxation spectrometer.

In the binary polymer solution consisting of a polymer and a small molecular weight solvent, owing to mutual diffusion arising from osmotic pressure fluctuations, the isotropic component of the light scattering spectrum is dominated by the concentration fluctuation. However, because of the mixing of the concentration fluctuation and viscoelasticity, the viscoelasticity that affects the mechanical properties of the polymer solution is also expected

to contribute to the dynamic light scattering spectrum. The effect of viscoelasticity on the dynamic light scattering spectrum of the binary polymer solution was recently analyzed by this author.^{2,3}

In depolarized light scattering (DLS), the scattered intensity arises from the anisotropy fluctuations of the dielectric constant tensor as a result of molecular reorientation.⁴ Because of the technological importance, attempts have been made to relate the DLS spectrum to the dynamic mechanical properties. Hess attempted to relate the DLS spectrum to the mechanical relaxation spectrum by using the Pockels photo-elastic law, in which the off diagonal part of the optical impermeability tensor is set proportional to the shear strain tensor.⁵ Since the Pockels photo-elastic law completely neglected the contribution due to molecular reorientation, it is only applicable to the description of the deformation of the condensed medium owing to acoustic waves at high frequency at which molecular reorientation fails to follow. In viscous molecular liquids, it is well known that reorientation of molecules makes a dominant contribution to the DLS intensity.^{6,7} In the viscoelastic region, both the molecular reorientation and overdamped shear waves contribute to the DLS spectral density and they can be probed by the dynamic light scattering technique.^{8,9} For viscoelastic liquids, such as polymer melts and polymer solutions, measurements of the dynamic shear modulus and compliance are of technological importance.¹⁰ It is thus of interest to find a method with which information concerning the dynamic shear compliance and shear modulus data can be extracted by the optical means using the DLS spectrum. Focusing on this objective, we present in this paper the result of a theoretical effort which succeeds in correlating the DLS spectrum with the dynamic shear compliance of a viscoelastic liquid. The experimental verification of the theoretical result will be the subject of our future publication. In section II we provide the theoretical

background needed for carrying out the analysis. In section III we consider the coupled motions of the off-diagonal part of the polarizability density and translation in the viscoelastic liquid. In section IV we show how the dynamic shear compliance can be obtained from the depolarized light scattering spectrum.

II. Theoretical Background

Consider a beam of electromagnetic radiation with wave vector \underline{k}_i and frequency ω_i propagating through a medium characterized by an anisotropic dielectric constant tensor $\underline{\epsilon}$ consisting of an average part $\bar{\epsilon}$ and a fluctuating part $\delta \underline{\epsilon}$.

The spectral power density of the scattered light $I_{si}(\underline{q}, \omega)$ is given by⁴

$$I_{si}(\underline{q}, \omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \alpha_{si}(\underline{q}, t) \alpha_{si}^*(\underline{q}) \rangle \quad (1)$$

where \underline{q} is the scattering vector given by $\underline{q} = \underline{k}_s - \underline{k}_i$; k_s is the amplitude of \underline{k}_s , the wave vector of the scattering light, and is equal to $2\pi n/\lambda_0$. Here n is the refractive index of the medium which is related to $\bar{\epsilon}$ by $n = (\bar{\epsilon})^{1/2}$; λ_0 is the wavelength of the incident light in vacuum. r is the radial distance from the scattering center to the detector. The quantity $\delta \epsilon_{si}(\underline{q}, \omega)$ is the projection of the fluctuating part of the dielectric constant tensor onto the incident light polarization indicated by \hat{n}_i and the scattered light polarization indicated by \hat{n}_s .

$\delta \epsilon_{si}(\underline{q}, \omega)$ is related to the polarizability density $\alpha_{si}(\underline{q}, \omega)$ by

$$\delta \epsilon_{si}(\underline{q}, \omega) = 4\pi \alpha_{si}(\underline{q}, \omega) \quad (2)$$

If the molecules are weakly coupled electronically, then the polarizability density tensor

component $\alpha_{si}(q,t)$ given above can be written as:

$$\alpha_{si}(q,t) = \sum_k \alpha_{si}^{(k)}(t) \exp \{i \underline{q} \cdot \underline{r}_k(t)\} \quad (3)$$

where $\alpha_{si}^{(k)}$ is the local field corrected polarizability tensor component of molecule k located at positions \underline{r}_k . Both $\alpha_{si}^{(k)}$ and \underline{r}_k depend on time because of molecular reorientation and translational diffusion. Owing to Eq. (3), measurements of the spectral power density $I_{si}(q,\omega)$ involving with different polarization vectors of the incident and scattered light beams will yield information about molecular motion in a dense fluid.

Using the scattering geometry with the incident light propagating along the x-axis and polarized along the y-axis of the laboratory coordinate system, it can be shown, for a system consisting of identical optically anisotropic molecules dissolved in an optically isotropic solvent, that the linear polarizability density involved in depolarized (VH) light scattering at wave vector \underline{q} has two components:⁴

$$\alpha_{VH}(q,t) = \alpha_{yz}(q,t) \cos(\theta/2) + \alpha_{yx}(q,t) \sin(\theta/2) \quad (4)$$

where θ is the scattering angle, and q is the amplitude of the scattering vector given by

$$\frac{4\pi n \sin(\theta/2)}{\lambda}. \text{ The expressions for } \alpha_{yz} \text{ and } \alpha_{xy} \text{ for molecules of arbitrary shape are most}$$

conveniently given in terms of rotational matrices.^{4,11} However, for optically symmetric top molecules, $\alpha_{yz}(q,t)$ and $\alpha_{xy}(q,t)$ are given by:

$$\alpha_{yz}(q,t) = \beta \sum_j n_y(j) n_z(j) e^{i \underline{q} \cdot \underline{r}_j} \quad (5)$$

$$\alpha_{xy}(q,t) = \beta \sum_j n_x(j) n_y(j) e^{i q \cdot \underline{r}_j} \quad (6)$$

where $\beta = \alpha_{\parallel} - \alpha_{\perp}$, α_{\parallel} and α_{\perp} being the components of the local field corrected molecular polarizability parallel and perpendicular to the symmetry axis, respectively. The position coordinate and orientation of the symmetry axis of molecule j are labeled by \underline{r}_j and $\hat{n}(j)$, respectively. The quantity $n_{\alpha}(j)$ is the projection of the unit vector representing the symmetry axis of molecule j onto the laboratory α -axis, $\alpha = x, y, z$. Both \underline{r}_j and $\hat{n}(j)$ are time dependent, but we do not explicitly write out the time dependence of \underline{r}_j and $n_{\alpha}(j)$ in Eqs (5) and (6) for brevity.

Using Eq. (4) one can readily show that the depolarized (VH) spectrum for a rotationally isotropic medium, is given by:

$$I_{VH}(q,\omega) = (1/2 \pi) \int_{-\infty}^{\infty} dt e^{-i\omega t} \{ \langle \alpha_{yz}(q,t) \alpha_{yz}^*(q) \rangle \cos^2(\theta/2) + \langle \alpha_{xy}(q,t) \alpha_{xy}^*(q) \rangle \sin^2(\theta/2) \} \quad (7)$$

where the cross terms, $\langle \alpha_{yz}(q,t) \alpha_{xy}^*(q) \rangle$ and $\langle \alpha_{xy}(q,t) \alpha_{yz}^*(q) \rangle$, do not contribute to the spectral intensity because of different reflection symmetry for α_{xy} and α_{yz} with respect to the yz plane. It should be noted that Eq. (9) is valid for molecules with arbitrary geometry, not being restricted to symmetry top molecules.

III. Coupling of Rotation and Translational Motions

In order to calculate the time correlation functions associated with the VH spectrum, we need to consider the types of molecular motion that affect the time dependence of $\alpha_{yz}(q,t)$ and $\alpha_{xy}(q,t)$. Andersen and Pecora¹² considered this problem in 1971 in the theory of the depolarized scattering spectrum from overdamped shear wave in a viscous molecular

liquid.¹¹ They used the symmetry consideration and concluded that the conserved hydrodynamic variables, such as number density and energy density will not couple to both α_{yz} and α_{yx} . However, because of identical reflection symmetry associated with the variables to P_y and α_{yz} , the y component of the linear momentum density P_y will couple to α_{yz} . From this, they then constructed a microscopic theory to describe the dynamics of the coupled variables using the technique of generalized hydrodynamics.¹²

To relate the viscoelastic effect to the depolarized light scattering spectrum of the fluid, we generalize in this paper the two-variable theory of Andersen-Pecora by including the memory effect in the relaxation kernel. We use a vector variable $A(\underline{q}, t)$ consisting of a set of two dynamic variables, one of which is $\alpha_{yz}(\underline{q}, t)$ and the other is $P_y(\underline{q}, t)$. As given by Eq. (2), the $\alpha_{yz}(\underline{q}, t)$ variable is related to the cooperative orientational motion of molecules within the scattering volume:

$$A(\underline{q}, t) = \begin{pmatrix} \alpha_{yz}(\underline{q}, t) \\ P_y(\underline{q}, t) \end{pmatrix} \quad (8)$$

where $P_y(\underline{q}, t)$ is the y-component of the linear momentum density given by:

$$P_y(\underline{q}, t) = \sum_j \pi_y^{(j)} e^{i \underline{q} \cdot \underline{r}_j} \quad (9)$$

Here $\pi_y^{(j)}$ is the y-component of the linear momentum of molecule j. The time dependence in $\pi_y^{(j)}$ and \underline{r}_j are not explicitly written out. For an isotropic fluid system, the physical property does not depend on the direction of \underline{q} ; only the amplitude is considered.

We need next to obtain an equation for the correlation function $\langle \alpha_{yz}(\underline{q}, t) \alpha_{yz}^*(\underline{q}) \rangle$ in order to calculate the depolarized light scattering spectrum. Having chosen the set of dynamic variable $A(\underline{q}, t)$, we can proceed to obtain the equations of motion for α_{yz} and P_y . Owing to the fact that α_{yz} is coupled to P_y we shall obtain two coupled equations. However,

in contrast to the treatment of Andersen-Pecora, we keep the memory effect in the generalized Langevin equations. The memory effect plays an important role in determining the viscoelasticity of the liquid. The various essential steps needed for obtaining the generalized Langevin equations for α_{yz} and P_y are given in the monograph by Wang,¹¹ and they are briefly described in Appendix I.

From Appendix I, the equations of motion for α_{yz} and P_y in the small q limit are given by:

$$\dot{\alpha}_{yz}(q,t) = -\int_0^t d\tau K_{11}(\tau) \alpha_{yz}(q,t-\tau) - iq \int_0^t d\tau K_{12}(\tau) P_y(q,t-\tau) \quad (10)$$

$$\dot{P}_y(q,t) = iq \int_0^t d\tau K_{21}(\tau) \alpha_{yz}(q,t-\tau) - q^2 \int_0^t d\tau K_{22}(\tau) P_y(q,t-\tau) \quad (11)$$

where the dots above α_{yz} and P_y indicate taking the time derivative. The explicit expressions for $K_{ij}(\tau)$ are given in Appendix I. In Eqs. (10) and (11), we have neglected the random force terms as these terms vanish upon taking the ensemble average with respect to the initial variables when calculating the time correlation functions. If the various $K_{ij}(\tau)$ terms relax significantly faster than the dynamic variables α_{yz} and P_y , then the Markov approximation can be used to simplify Eqs (10) and (11). If the Markov approximation is assumed, then Eqs (10) and (11) reduce to:

$$\dot{\alpha}_{yz}(q,t) = -\Gamma \alpha_{yz}(q,t) - iq\mu P_y(q,t) \quad (12)$$

$$\dot{P}_y(q,t) = -\frac{q^2 \eta_s}{\rho_m} P_y(q,t) + iq\mu' \alpha_{yz}(q,t) \quad (13)$$

where Γ is the orientational relaxation rate equal to the time integral of $K_{11}(\tau)$; ρ_m is the

mass density and η_s is the shear viscosity of the liquid which is proportional to the time integral of $K_{22}(\tau)$; μ and μ' are rotation-translation coupling constants associated with the time integrals of $K_{12}(\tau)$ and $K_{21}(\tau)$, respectively. Equations (12) and (13) are equivalent to the equations used by Anderson and Pecora for the calculation of the depolarized light scattering spectrum of the viscous molecular liquid.¹² Since we do not assume the Markov approximation in the present work, the viscoelastic response of the liquid is retained in Eqs (10) and (11).

To proceed, we need to solve the coupled equation given by Eqs. (10) and (11). These are coupled differential-integral equations of the convolution type and can be solved by using the usual Laplace transform technique.

Taking the Laplace transform of Eqs (10) and (11) and after rearranging, we obtain:

$$\begin{bmatrix} s + \hat{K}_{11} & iq\hat{K}_{12} \\ -iq\hat{K}_{21} & s + q^2\hat{K}_{22} \end{bmatrix} \begin{bmatrix} \hat{\alpha}_{yz}(q,s) \\ \hat{P}_y(q,s) \end{bmatrix} = \begin{bmatrix} \alpha_{yz}(q) \\ P_y(q) \end{bmatrix} \quad (14)$$

where $\hat{\alpha}_{yz}(q,s)$ and $\hat{P}_y(q,s)$ are the Laplace transform of $\alpha_{yz}(q,t)$ and $P_y(q,t)$, respectively. They are given by:

$$\hat{\alpha}_{yz}(q,s) = \int_0^\infty \alpha_{yz}(q,t) e^{-st} dt \quad (15a)$$

$$\hat{P}_y(q,s) = \int_0^\infty P_y(q,t) e^{-st} dt \quad (15b)$$

To obtain the correlation functions, we first invert Eq. (14) to obtain the solution. We next multiply $\hat{\alpha}_{yz}(q,s)$ by its initial value $\alpha_{yz}^*(q)$, and $\hat{P}_y(q,s)$ by its initial value $P_y^*(q)$ and then take the ensemble averages for both of them. The results are:

$$\dot{C}_a^{yz}(q,s) \equiv \langle \dot{\alpha}_{yz}(q,s) \alpha_{yz}^*(q) \rangle = \frac{1}{\Delta(q)} (s + q^2 \hat{K}_{22}) kT \chi_a \quad (16a)$$

$$\dot{C}_p(q,s) \equiv \langle \dot{P}_y(q,s) P_y^*(q) \rangle = \frac{1}{\Delta(q)} (s + \hat{K}_{11}) Nm kT \quad (16b)$$

where N is the total number of molecules and m is the mass of the molecules. The other quantities are given by:

$$\Delta(q) = (s + \hat{K}_{11})(s + q^2 \hat{K}_{22}) - q^2 \hat{K}_{12} \hat{K}_{21} \quad (17a)$$

$$\hat{K}_{11}(s) = \frac{1}{kT \chi_a} \int_0^\infty dt e^{-st} \langle \dot{\alpha}_{yz}(t) \dot{\alpha}_{yz}^*(0) \rangle_Q \equiv \Gamma(s) \quad (17b)$$

$$\hat{K}_{22}(s) \equiv \frac{1}{V kT} \int_0^\infty dt e^{-st} \langle \sigma_{yz}(t) \sigma_{yz}^*(0) \rangle \equiv \hat{\eta}(s) / \rho_m \quad (17c)$$

We can combine $\hat{K}_{12}(s)$ and $\hat{K}_{21}(s)$ and introduce a quantity $\zeta(s)$:

$$-\hat{K}_{12}(s) \hat{K}_{21}(s) \equiv \zeta(s) \Gamma(s) / \rho_m \quad (17d)$$

The quantity $\zeta(s)$ has the same dimension of viscosity and will be referred to as the dynamic coupling viscosity as its presence arises from rotation-translational coupling. The dynamic coupling viscosity ζ is easily shown to be given by:

$$\zeta(s) = \frac{1}{V \Gamma(s) (kT \chi_a) kT} \left| \int_0^\infty dt e^{-st} \langle i \sigma_{yz}(t) \alpha_{yz}(0) \rangle_Q \right|^2 \quad (18e)$$

The quantity χ_a appearing in Eqs (17b) and (17e) is the static polarizability susceptibility defined in Appendix I.

IV. Depolarized Light Scattering Spectrum and Dynamic Modulus

We now relate $\hat{\eta}(s)$ to the dynamic shear (stress) modulus $G^*(\omega)$. Using Eqs (16a) and (17c) and setting $s = i\omega$, we can rewrite the momentum density correlation function given in Eq. (16b) as:

$$\hat{C}_p(q, i\omega) = \frac{Nm kT}{[i\omega + (q^2/\rho_m)\hat{\eta}] + [q^2\zeta\Gamma/\rho_m]/[i\omega + \Gamma]} \quad (18)$$

At zero frequency, the dynamic coupling viscosity ζ vanishes, and one obtains the limiting hydrodynamic result for all molecular fluids:

$$\lim_{\omega \rightarrow 0} \hat{C}_p(q, i\omega) = (Nm kT)/(q^2/\rho_m)\eta_s \quad (19)$$

where η_s is the macroscopic shear viscosity equal to:¹³

$$\eta_s = \lim_{\omega \rightarrow 0} [G''(\omega)/\omega] \quad (20)$$

At finite frequency, the dynamic coupling viscosity is finite, and from Eqs.(18) and (19) we expect that

$$[\hat{\eta}(i\omega) + \zeta(i\omega)] = \hat{G}(\omega) \quad (21)$$

where $\hat{G}(\omega)$ is related to the dynamic shear modulus G^* by; $i\omega \hat{G}(\omega) = G^*(\omega)$. The dynamic modulus can be separated into a real $G'(\omega)$ and an imaginary part $G''(\omega)$:

$$G^*(\omega) = G'(\omega) + iG''(\omega) = i\omega \int_0^\infty dt e^{-i\omega t} G(t) \quad (22)$$

In the limit of small frequency, as given by Eq (20) $G''(\omega)/\omega$ becomes the macroscopic viscosity but $G'(\omega)/\omega$ vanishes.¹³

On the account of Eq. (21), we can rewrite Eq. (17a) as:

$$\Delta(i\omega) = (i\omega + \Gamma) \left(i\omega + \frac{q^2}{\rho_m} \hat{G} - \frac{q^2}{\rho_m} \frac{i\omega \zeta}{i\omega + \Gamma} \right) \quad (23)$$

and

$$C_{\alpha}^{yz}(i\omega) = \frac{[i\omega + (q^2/\rho_m)(\hat{G} - \zeta)] kT\chi_{\alpha}}{(i\omega + \Gamma)[i\omega + (q^2/\rho_m)\hat{G} - (q^2/\rho_m)[i\omega\zeta/(i\omega + \Gamma)]]} \quad (24)$$

We expect in general the dynamic coupling viscosity ζ to be much less than the dynamic shear viscosity \hat{G} . Thus, we proceed by expanding Eq. (24) in power series of ζ/\hat{G} , and retain only the linear term in ζ to arrive at:

$$C_{\alpha}^{yz}(i\omega) = \left\{ \frac{1}{i\omega + \Gamma} - \left(\frac{q^2}{\rho_m} \right) \frac{\zeta\Gamma}{(i\omega + \Gamma)^2 [i\omega + (q^2/\rho_m)\hat{G}]} \right\} kT\chi_{\alpha} \quad (25)$$

For the fluid in the viscoelastic regime, the macroscopic viscosity is high so that the molecular reorientation rate is slow. In addition, we shall also neglect the dispersion of the collective reorientation rate Γ and the dynamic coupling viscosity ζ ; i.e. we shall assume that Γ and ζ are real and independent of frequency in the frequency window of the dynamic light scattering experiment. This assumption is justified experimentally.⁹

We now combine Eq. (25) with the xy component of the scattering spectrum (c.f. Eq. (7)) and obtain for $\omega > \Gamma$, the spectral power density of the depolarized Rayleigh scattered light as:

$$S_{\text{vH}}(q, \omega) = I_{\text{vH}}(q, \omega)/(kT\chi_a) \\ = \frac{\Gamma}{\omega^2 - \Gamma^2} + \left(\frac{q^2}{\rho_m}\right)\left(\frac{\Gamma}{\omega^2}\right) \cos^2 \frac{\theta}{2} \operatorname{Re} \left\{ \frac{i\omega\zeta}{-\omega^2 + q^2 G^*(\omega)/\rho_m} \right\} \quad (26)$$

where $G^*(\omega)$ is the dynamic shear modulus given in Eq. (22); the symbol Re indicates taking the real part of the expression within the curly brackets.

One notes in Eq. (26), and more generally Eq. (18), the fact that the dynamic shear modulus enters the depolarized scattering spectrum is due entirely to the presence of rotation-translational coupling. If the dynamic coupling viscosity ζ vanishes, then the depolarized spectrum becomes a simple Lorentzian, with the half-width at the half-height equal to Γ , the collective reorientational rate. This is consistent with the previous result.^{6,7} For the viscoelastic liquid, the molecular reorientation rate is slow and the Lorentz term is very narrow. In addition, one also notes that the second term in Eq.(26) containing the dynamic shear modulus term is proportional to $\cos^2 \theta/2$. Thus, the dynamic shear modulus contribution is pronounced at small scattering angles, but it vanishes when the scattering angle θ equals 180° . However, except for low frequencies, one notes that the second term is proportional to q^2 , it also becomes small at small scattering angle. Hence, when the factors of q^2 and $\cos^2 \theta/2$ are combined, one arrives at the conclusion that $\theta = 90^\circ$ is the optimum scattering angle to observe the shear modulus contribution to the depolarized scattering spectrum. However, if frequencies are low, the q^2 factor is canceled out by the q^2 term in the denominator and in this situation the DLS spectrum becomes independent of the scattering angle. But, due to the $\cos^2 \theta/2$ factor, the intensity of the scattered light associated with the shear modulus is most pronounced at small scattering angle.

Returning to Eq. (26), we separate G^* into real and imaginary parts. By taking the real part of Eq. (26) and after carrying out some algebra, we obtain the DLS spectrum as:

$$S_{\text{VH}}(q, \omega) = \frac{\Gamma}{\omega^2 + \Gamma^2} + \left(\frac{q^2}{\rho_m}\right) \zeta \Gamma \left(\cos^2 \frac{\theta}{2}\right) \left(\frac{1}{\omega}\right) \frac{(q^2/\rho_m)G''}{(-\omega^2 + q^2 G'/\rho_m)^2 + (q^2 G''/\rho_m)^2} \quad (27)$$

If the depolarized light scattering experiment is carried out by using an electronic correlator, whose dynamic range is usually less than 1 MHz, then for polymer solutions with a storage modulus greater than 10^2 Pa , the conditions $q^2 G'/\rho_m \gg \omega^2$ is valid over the entire dynamic range of the correlator. In such a circumstance, the term ω^2 in the denominator of the second term of Equation (27) can be neglected, and as a result, Eq. (27) reduces to:

$$S_{\text{VH}}(q, \omega) = \frac{\Gamma}{\omega^2 + \Gamma^2} + \zeta \Gamma \left(\cos^2 \frac{\theta}{2}\right) J''(\omega)/\omega \quad (28)$$

where $J''(\omega)$ is the imaginary part of the dynamic shear compliance, given by

$$J''(\omega) = \frac{G''(\omega)}{[G'(\omega)]^2 + [G''(\omega)]^2} \quad (29)$$

Using the definition of $J''(\omega)$,¹⁰ we can transform Eq. (28) back to the time domain as:

$$g_{\text{VH}}(q, t) = e^{-\Gamma t} + \zeta \Gamma \left(\cos^2 \frac{\theta}{2}\right) [J_e^0 - J(t)] \quad (30)$$

where J_e^0 is the steady state shear compliance, and $J(t)$ is the shear creep compliance. $g_{\text{VH}}(q, t)$ is the normalized VH polarizability correlation function. Modern dynamic light scattering experiments often employ a digital electronic correlator and directly measures the time correlation function $g_{\text{VH}}(q, t)$. Equation (30) is more convenient than Eq. (28) which deals with the spectral power density.

Equation (28) or Eq. (30) is an important result; it shows that the dynamic shear compliance can be obtained from the DLS spectrum. Owing to the presence of rotation-translation coupling, the DLS spectrum of an optically anisotropic viscoelastic liquid will consist of two components. One is associated with reorientational motion, and the other with the viscoelasticity of the liquid. The viscoelastic component is proportional to the

imaginary part of the dynamic shear compliance. This result is quite analogous to that previously obtained for the polarized scattering spectrum, in which it is shown that the density fluctuation spectrum as probed in isotropic scattering is proportional to the imaginary part of the dynamic compression compliance.¹ However, due to the presence of reorientation motion which in some cases contributes significantly to the DLS intensity, the depolarized light scattering spectrum is proportional to the imaginary part of the dynamic shear compliance only if the collective reorientation rate Γ is so small that it can be neglected. If the reorientational rate is neglected, then one obtains a result identical to that obtained by using the photo-elastic law,⁵ and the factor $\zeta\Gamma$ becomes the Pockels' photoelastic constant.

If the reorientational dynamics contributes to depolarized light scattering, then the reorientational effect has to be separated out in order to use depolarized light scattering as a technique to obtain the dynamic shear compliance data. To separate the reorientational contribution to the spectrum, one can first carry out the DLS experiment at large scattering angle near 180° . As one notes in Eq. (28), the spectrum at large scattering angle is mainly due to reorientation. After obtaining the angular independent, the reorientational spectrum (or the correlation function, Eq. (30)) can be subtracted off from the total DLS spectrum to obtain the viscoelastic spectrum.

An alternative method can also be used. This method allows one to obtain both the real and imaginary parts of the dynamic shear compliance spectrum. We now describe this alternative method of separating the reorientational contribution to obtain the compliance spectrum.

From Eq. (16a) we take the inverse of $\hat{C}_\alpha^{yz}(q,s)$ and obtain by setting $s = i\omega$,

$$\frac{kT\chi_a}{\int_0^\infty dt e^{-i\omega t} C_a^{yz}(q,t)} = i\omega + \Gamma + \left(\frac{q^2 \zeta \Gamma}{\rho_m}\right) \frac{i\omega}{-\omega^2 + (q^2/\rho_m)G^*} \quad (31)$$

To obtain Eq. (31), we also neglect the higher order terms in ζ due to the fact that ζ is in general much less than \hat{G} .

We next write the one sided Fourier transform of the polarizability time correlation function appearing in Eq. (31) as:

$$\frac{1}{kT\chi_a} \int_0^\infty dt e^{-i\omega t} C_a^{yz}(q,t) = I(q,\omega) - iH(q,\omega) \quad (32)$$

Here $I(q,\omega)$ and $H_{yz}(q,\omega)$ are the cosine and sine transforms of the normalized correlation function $C_a^{yz}(q,t)$, respectively. The cosine transform of $C_a^{yz}(q,t)$ is proportional to the yz component of the depolarized light spectrum given in Eq. (7).

Using Eq. (32) and expressing G^* in terms of real and imaginary parts, we obtain from Eq. (31)

$$\frac{1}{I(q,\omega) - iH(q,\omega)} = i\omega + \Gamma + \left(\frac{q^2 \zeta \Gamma}{\rho_m}\right) \frac{i\omega}{-\omega^2 + \left(\frac{q^2}{\rho_m}\right)(G' + iG'')} \quad (33)$$

Equating the real and imaginary parts on both sides of Eq. (36) and also neglecting the ω^2 term, we obtain for the real part

$$A(\omega) \equiv \frac{I}{I^2 + H^2} = \Gamma + \omega \zeta \Gamma J''(\omega) \quad (34)$$

and for the imaginary part

$$B(\omega) \equiv \frac{H}{I^2 + H^2} = \omega + \omega \Gamma \zeta J'(\omega) \quad (35)$$

where the frequency dependence for I and H in Eqs. (33) and (34) are not written out explicitly; J' and J'' are real and imaginary parts dynamic shear compliance $J^*(\omega)$, given by

$$J^*(\omega) = J'(\omega) - iJ''(\omega) \quad (36)$$

Dynamic shear modulus $G^*(\omega)$ and dynamic shear compliance $J^*(\omega)$ are related by the equation¹⁰

$$J^*(\omega)G^*(\omega) = 1 \quad (37)$$

One notes that $B(\omega)$ vanishes at $\omega = 0$. Equations (34) and (35) can be used to separate the reorientational rate Γ from the DLS spectrum. The method consists of computing the sine and cosine transforms of the polarizability correlation function that one measures by using a digital electronic correlator. From these one can calculate $A(\omega)$ and $B(\omega)$. From the plots of $A(\omega)$ as a function of ω one obtains Γ , as an intercept. After obtaining Γ , one can substitute it into Eqs. (34) and (35) to calculate $\zeta J''$ and $\zeta J'$ as a function of frequency.

However, as one notes in Eq. (7), the depolarized Rayleigh spectrum has two components. The component proportional to the $\sin^2 \theta/2$ term is only associated with the rotational dynamics. The contribution of this term must be either subtracted off or minimized in order to use the results given in Eqs. (34) and (35). This can be accomplished by carrying out the DLS experiment at a small scattering angle.

In conclusion, we show that it is possible to use the method of the DLS experiment to obtain J' and J'' or $J(t)$ of a viscoelastic liquid. We have used the generalized Langevin equations to analyze the connection between the DLS spectrum and dynamic shear compliance. We have shown that, owing to rotation-translational coupling, both reorientational motion and viscoelasticity contribute to the DLS spectrum. In the limit of negligible molecular reorientation, the DLS spectrum is shown to be proportional to the imaginary part of the dynamic compliance spectrum, a result predicted by the photoelastic law. When both the reorientational motion and viscoelasticity contribute to the DLS

intensity, we have provided methods for separating the reorientational component from the DLS spectrum to obtain the dynamic shear compliance data.

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Appendix I

Generalized Hydrodynamic Theory of Coupling of Rotational

Motion to Shear Waves

Given the coupled dynamic variables $\alpha_{yz}(q,t)$ and $P_y(q,t)$ defined in Eqs. (3) and (9), we express then as a column matrix $\underline{A}(q,t)$.

$$\underline{A}(q,t) = \begin{bmatrix} \alpha_{yz}(q,t) \\ P_y(q,t) \end{bmatrix} \quad (\text{A-1})$$

where in $\alpha_{yz}(q,t)$ is the yzth component of the polarizability density tensor. Its time dependence is due to translation and it describes the reorientational motion of a collection of molecules inside the scattering volume. $P_y(q,t)$ is the y component of the linear momentum density for the collection of molecules inside the scattering volume. We follow the technique of generalized hydrodynamic theory and obtain the generalized Langevin equation of motion for $\underline{A}(q,t)$ as

$$\frac{\partial}{\partial t} \underline{A}(q,t) = i\hat{\Omega} \cdot \underline{A}(q,t) - \int_0^t \hat{K}(q,\tau) \cdot \underline{A}(q,t-\tau) d\tau + \underline{F}(q,t) \quad (\text{A-2})$$

In Eq. (A-2), $\hat{\Omega}$ is the frequency matrix, and is a null matrix for the chosen set of dynamic variables given in Eq. (A-1).⁴ $\hat{K}(q,\tau)$ is the relaxation matrix given by:

$$\hat{K}(q,\tau) = \langle \underline{F}(q,\tau) \underline{F}^*(q) \rangle \langle \underline{A} \underline{A}^* \rangle^{-1} \quad (\text{A-3})$$

where $\underline{F}(q,\tau)$ is the random force which can be calculated according to:

$$\underline{F}(q,t) = e^{i(1-p)\hat{A}}(i-p) \begin{bmatrix} i\mathcal{L}\alpha_{yz}(q) \\ i\mathcal{L}P_y(q) \end{bmatrix} = \begin{bmatrix} F_\alpha(q,t) \\ F_p(q,t) \end{bmatrix} \quad (A-4)$$

and

$$\langle \underline{A} \underline{A}^\dagger \rangle^{-1} = \begin{bmatrix} \langle |\alpha_{yz}(q)|^2 \rangle^{-1} & 0 \\ 0 & 1/NmkT \end{bmatrix} \quad (A-5)$$

where ϕ is the Liouville operation and p is the projection operator. Since

$$F_\alpha(q) = i\mathcal{L}\alpha_{yz}(q) = \sum_j [\dot{\alpha}_{yz}^{(0)} + iq(\pi_z^{(0)}/m_j)\alpha_{yz}^{(0)}]e^{iq \cdot r_j} \quad (A-6)$$

and from the momentum conservation equation, we have

$$F_p(q) = i\mathcal{L}P_y(q) = \frac{\partial}{\partial t} P_y|_{t=0} = iq\sigma_{yz}(q) \quad (A-7)$$

In the small q limit, the stress tensor σ_{yz} becomes q -independent, and is given by

$$\sigma_{yz} = \sum_j [\pi_y^{(0)} z_j + \pi_y^{(0)} \pi_z^{(0)}/m] \quad (A-8)$$

and the initial values of $F_\alpha(q)$ and $F_p(q)$ become

$$F_\alpha(q) = \sum_j \dot{\alpha}_{yz}^{(0)} e^{iq \cdot r_j} \quad (A-9)$$

and

$$F_p(q) = iq\sigma_{yz} \quad (A-10)$$

Using Eqs. (A-4), (A-5), (A-9) and (A-10), we obtain from Eq. (A-3) the relaxation matrix $\underline{K}(q, \tau)$ in the limit of small q as

$$\underline{K}(\tau) = \begin{bmatrix} K_{11}(\tau) & -iqK_{12}(\tau) \\ iqK_{21}(\tau) & q^2K_{22}(\tau) \end{bmatrix} \quad (A-11)$$

where in the limit of small q ,

$$K_{11}(\tau) = \langle \dot{\alpha}_{yz}(\tau) \dot{\alpha}_{yz}^*(0) Q \rangle / kT\chi_a \quad (A-12)$$

with

$$kT\chi_a \equiv \langle |\sum_j \alpha_{yz}^{\oplus}|^2 \rangle \quad (A-13)$$

$$K_{12}(\tau) = \langle \dot{\alpha}_{yz}(t) (i\sigma_{yz})^* \rangle / Nm kT \quad (A-14)$$

$$K_{21}(\tau) = \langle i\sigma_{yz}(t) \dot{\alpha}_{yz}^*(t) \rangle / kT\chi_a \quad (A-15)$$

and

$$K_{22}(\tau) = \langle \sigma_{yz}(t) \sigma_{yz}^* \rangle / Nm kT \quad (A-16)$$

Here the subscript Q in Eq (A-12) designates that the time dependence is taken with respect to projected Liouville space.

If we write down from Eq. (A-2) the equation for each individual dynamic variable, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \alpha_{yz}(q,t) = & - \int_0^t d\tau K_{11}(\tau) \alpha_{yz}(q,t-\tau) - iq \int_0^t d\tau K_{12}(\tau) P_y(q,t-\tau) \\ & + F_a(q,t) \end{aligned} \quad (A-17)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} P_y(q,t) = & iq \int_0^t d\tau K_{21}(\tau) \alpha_{yz}(q,t-\tau) - q^2 \int_0^t d\tau K_{22}(\tau) P_y(q,t-\tau) \\ & + F_p(q,t) \end{aligned} \quad (A-18)$$

which are equivalent to Eqs. (13) and (14) provided that the random force terms $F_a(q,t)$ and $F_p(q,t)$ are neglected.

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